US007749906B2

(12) **United States Patent**
Dominguez et al.

(10) **Patent No.:** **US 7,749,906 B2**
(45) **Date of Patent:** **Jul. 6, 2010**

(54) **USING UNSTABLE NITRIDES TO FORM SEMICONDUCTOR STRUCTURES**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 1171 days.

(21) Appl. No.: **11/359,060**

(22) Filed: **Feb. 22, 2006**

(65) **Prior Publication Data**

US 2007/0194287 A1 Aug. 23, 2007

(51) **Int. Cl.**
H01L 21/44 (2006.01)

(52) **U.S. Cl.** **438/687**; 257/E21.006

(58) **Field of Classification Search** 438/652–654, 438/687, 775; 257/E21.006
See application file for complete search history.

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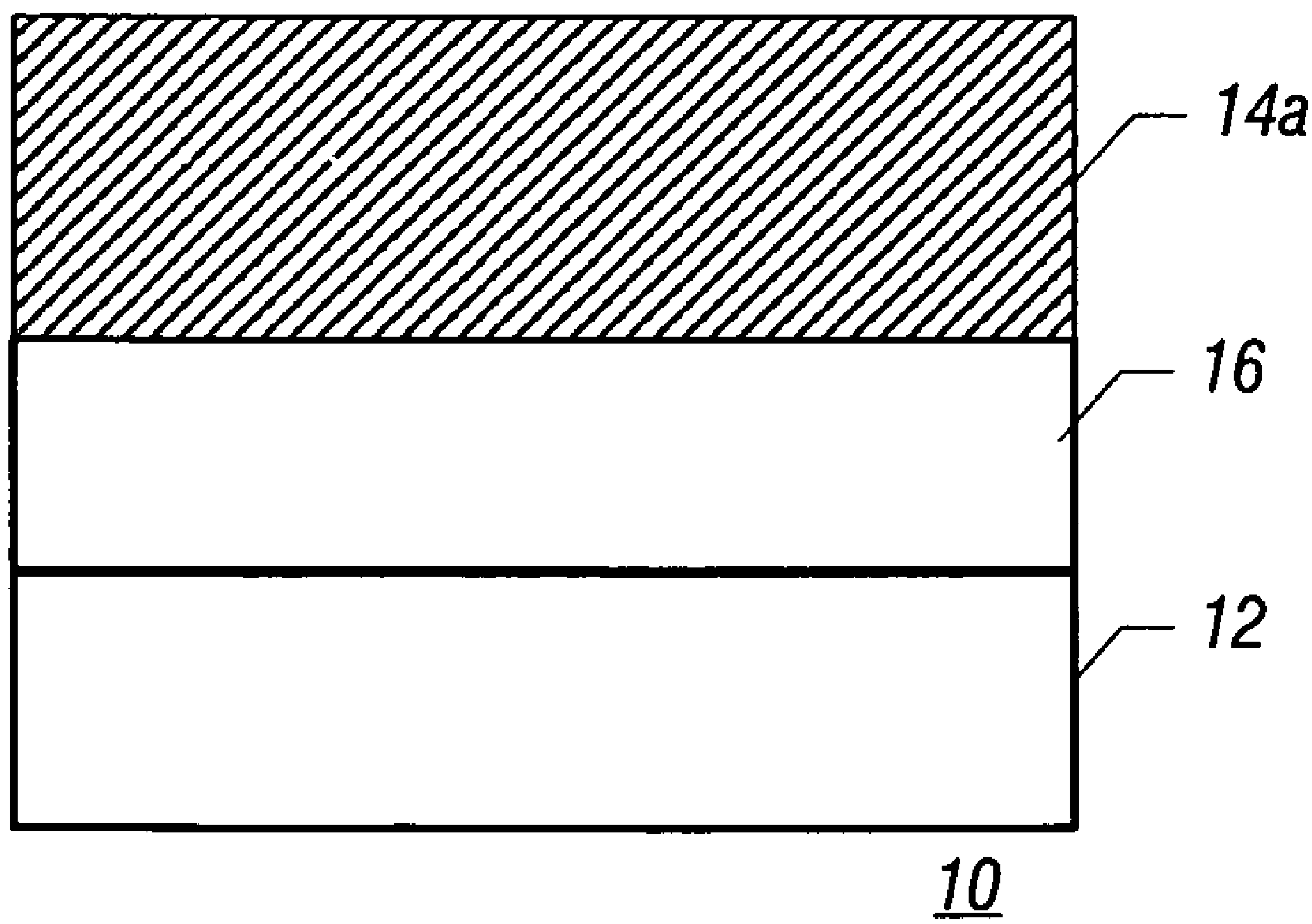
(57) **ABSTRACT**

Incompatible materials, such as copper and nitrided barrier layers, may be adhered more effectively to one another. In one embodiment, a precursor of copper is deposited on the nitrided barrier. The precursor is then converted, through the application of energy, to copper which could not have been as effectively adhered to the barrier in the first place.

17 Claims, 2 Drawing Sheets



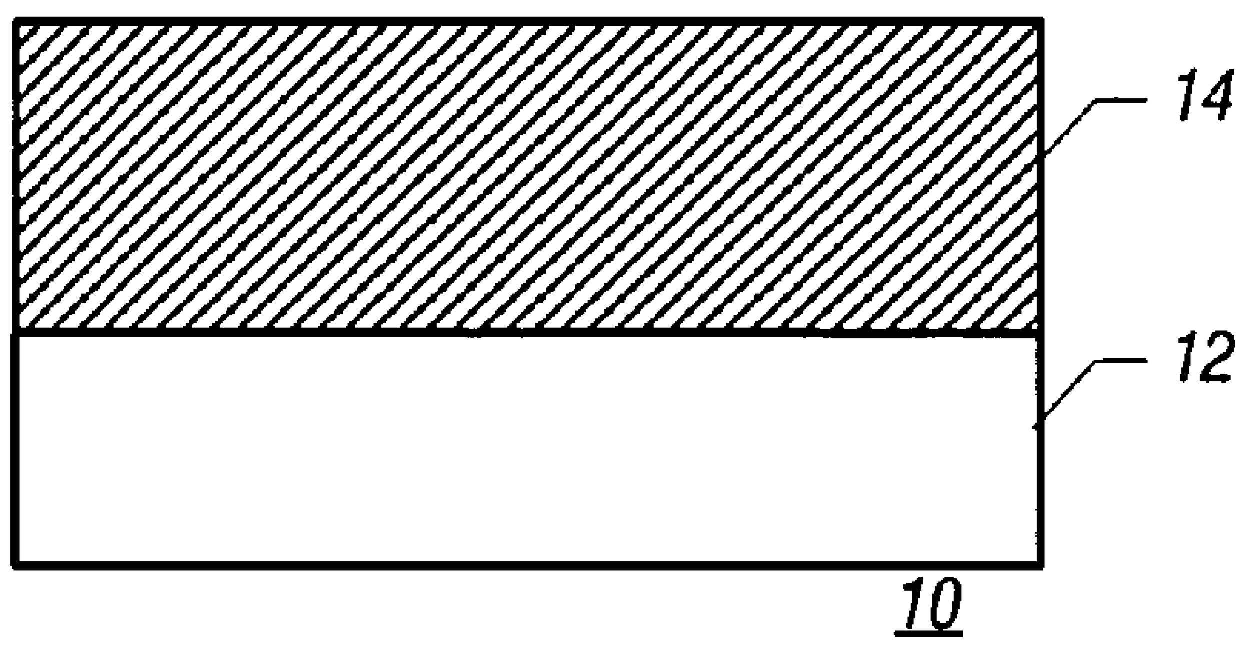


FIG. 1

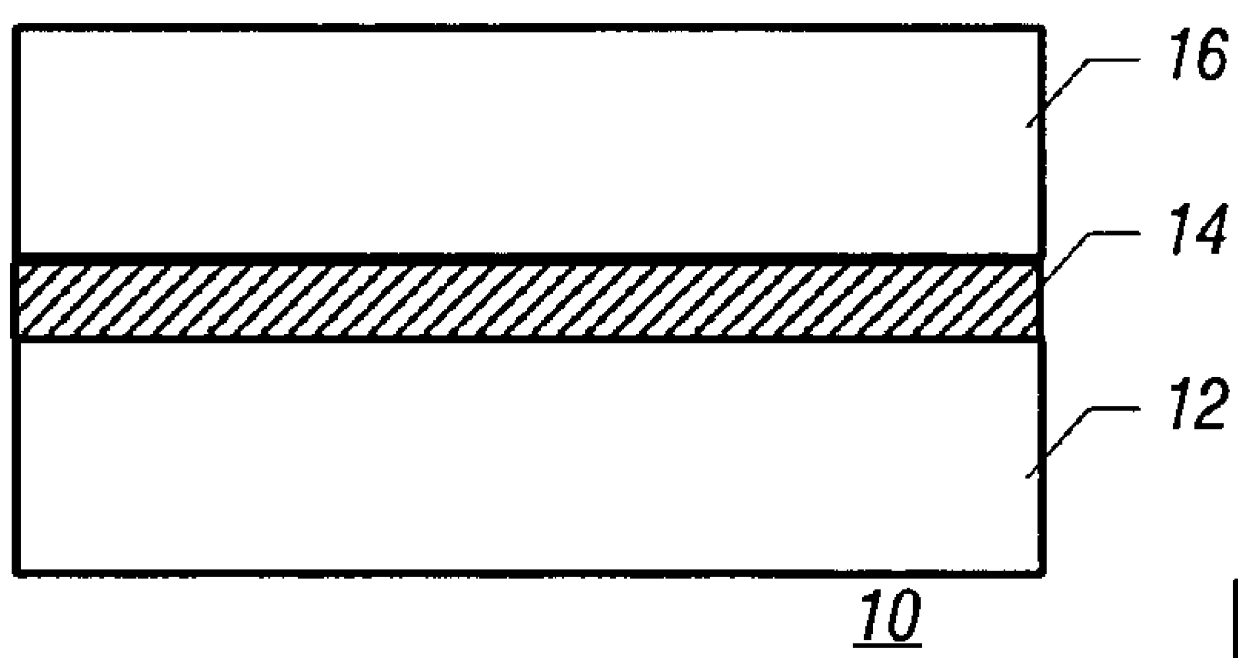


FIG. 2

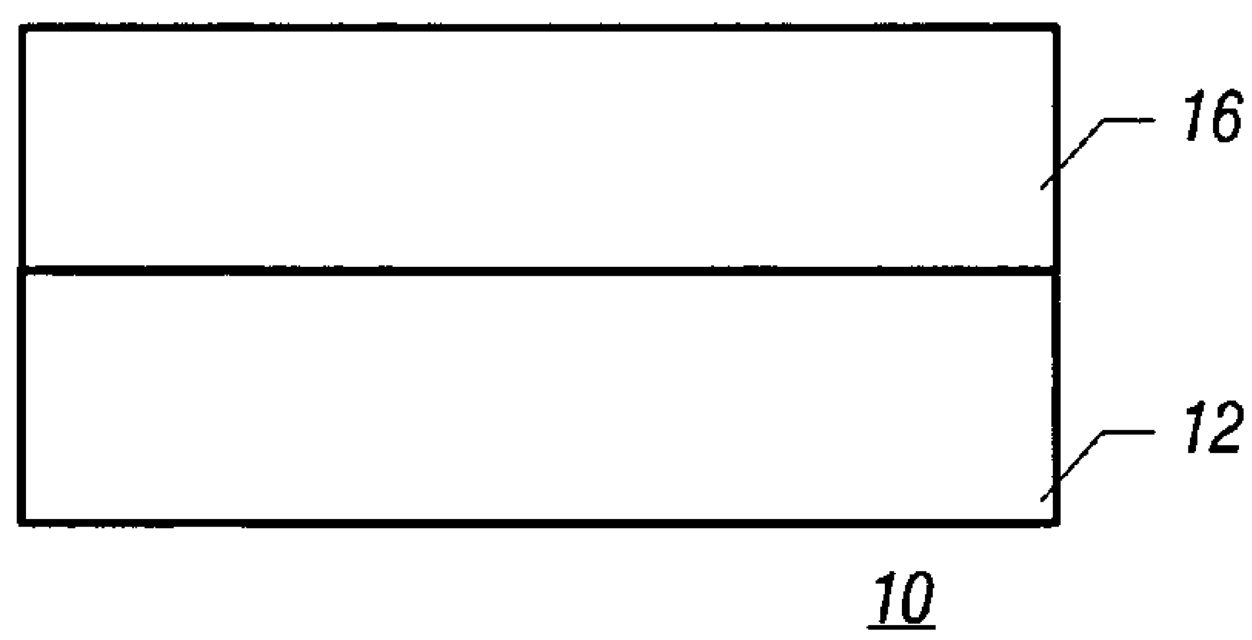


FIG. 3

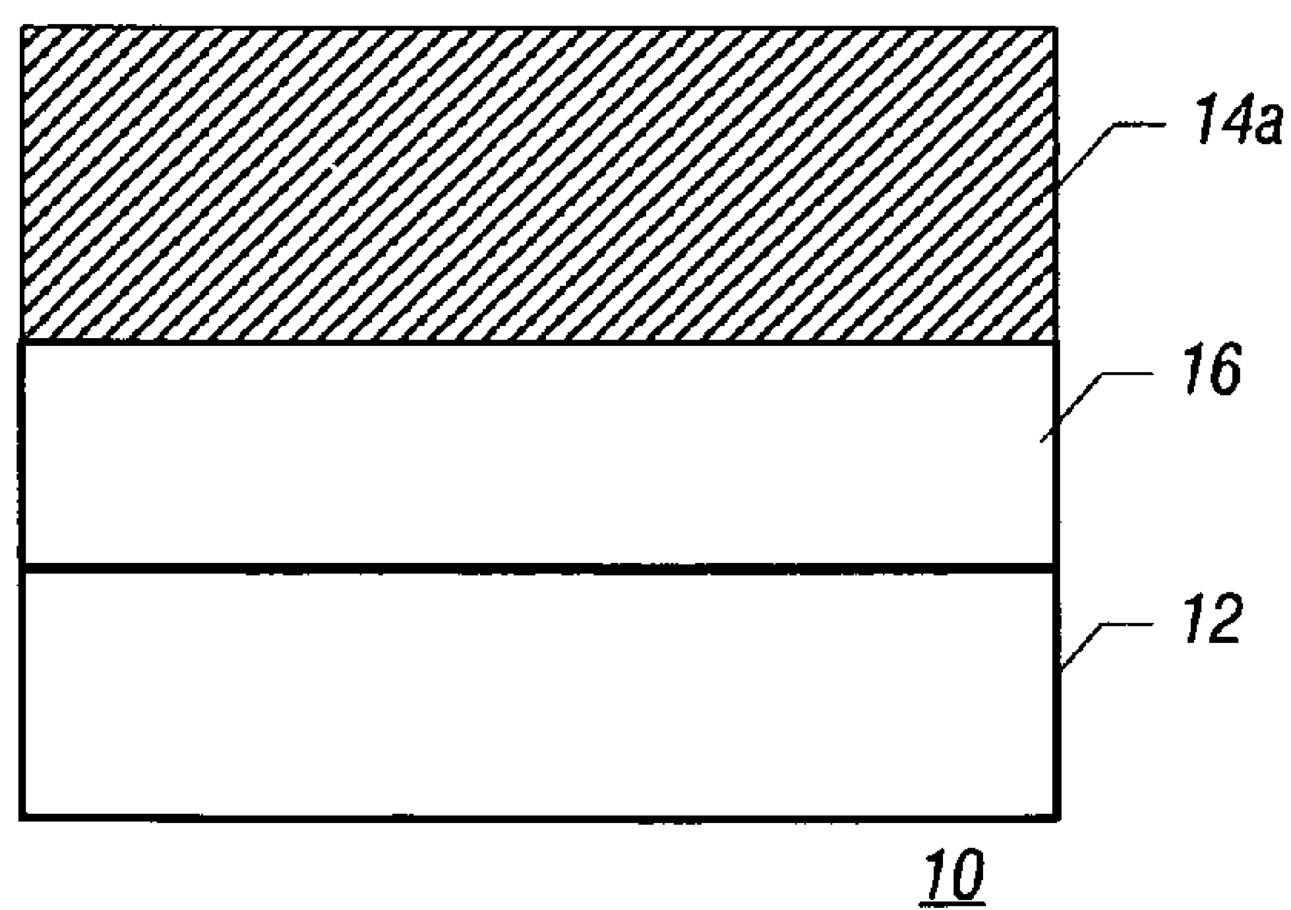


FIG. 4

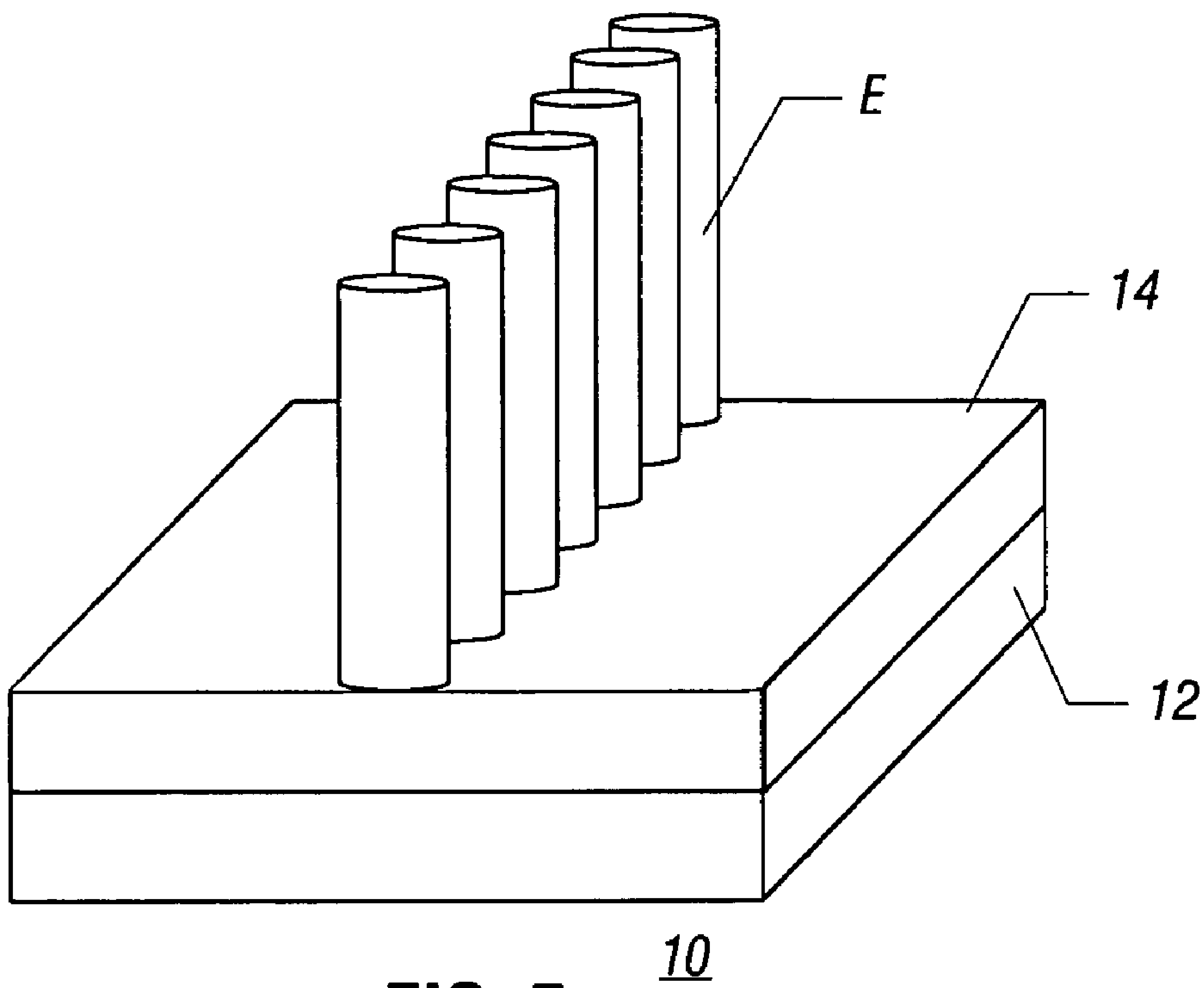


FIG. 5

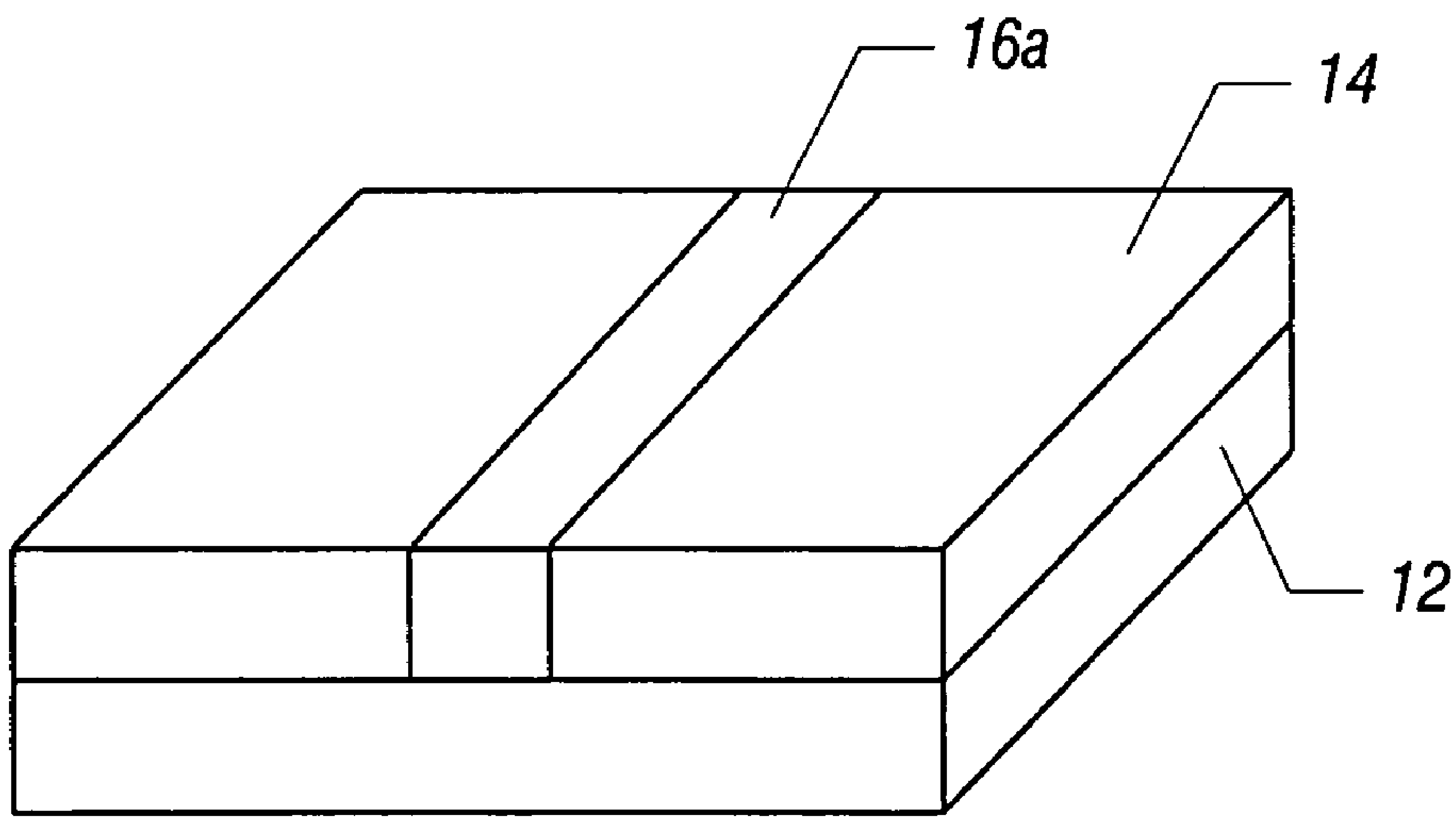


FIG. 6

USING UNSTABLE NITRIDES TO FORM SEMICONDUCTOR STRUCTURES

BACKGROUND

This invention relates generally to the fabrication of integrated circuits.

In the fabrication of integrated circuits, it is desirable to use a variety of different materials over a variety of different substrates. Sometimes materials that an engineer would like to use over a given substrate are incompatible with that substrate. By "incompatible" it is intended to mean that the upper material cannot be deposited onto the lower layer with sufficient adherence to the lower layer to avoid delamination.

Thus, commonly, in order to adhere these incompatible layers to one another, special deposition techniques are required or adhesion layers must be provided between the incompatible layers.

It is also desirable in a variety of applications to form nanowires or very small electrical conductors in semiconductor integrated circuits. Commonly, the deposition of such small conductors is extremely difficult. Moreover, to form a conductor, such as a copper conductor buried in other material, involves a large and cost ineffective number of process steps.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is an enlarged, cross-sectional view at an early stage of manufacture according to one embodiment;

FIG. **2** is an enlarged, cross-sectional view at a subsequent stage of manufacture according to one embodiment;

FIG. **3** is an enlarged, cross-sectional view at a stage subsequent to the stage shown in FIG. **1** according to one embodiment;

FIG. **4** is an enlarged, cross-sectional view at a subsequent stage to FIG. **3** in accordance with one embodiment of the present invention;

FIG. **5** is an enlarged, cross-sectional view of another embodiment of the present invention; and

FIG. **6** is an enlarged, cross-sectional view of still another embodiment of the present invention.

DETAILED DESCRIPTION

Referring to FIG. **1**, a layer of a first material **12**, over a substrate or wafer **10**, may receive on its upper surface a deposit of a second material **14**. The material **14** and the material **12** may be sufficiently compatible that adequate adherence can be obtained between the materials **12** and **14** in some embodiments. However, the material **14**, now adhered to the material **12**, may then be converted to another material incompatible with the material **12** if directly deposited on the material **12**. By depositing the material **14** in a first form and then converting it into a second form, the incompatible material may be successfully adhered to the first material **12**.

As an example, the material **12** may be a nitrided barrier layer such as titanium nitride or tungsten nitride. The material **14**, in one embodiment, may be an unstable metal nitride, such as Cu_3N or Cu_4N, as two examples. As another example, the material **14** may be Ni_3N.

In one embodiment, the material **14** is deposited by a atomic layer deposition (ALD) and/or chemical vapor deposition (CVD). Precursors may be used to deposit the unstable metal nitrides by ALD or CVD, including, but not limited to, copper amidinate variants, betadiketiminates, azaallyls, betadiketonates, pyridines, cyclic arenes, and alkenes. Deposition of the material **14** may take place at a substrate temperature between 80° C. and 150° C., under chamber pressures between 100 mTorr to 10 Torr, in some embodiments. Co-reactants may be pulsed or flown to form unstable metal nitrides such as Cu_3N or Cu/Cu_3N mixtures. The co-reactants may include, but are not limited to, NH_3, primary amines, secondary amines, tertiary amines, hydrazine, BR3-amine adducts (where R is alkyl, proton or both and the amine is primary, secondary, tertiary), azides, as well as pure nitrogen, nitrogen plasma, or N_2/H_2 plasma, as well as any plasma and combinations from aforementioned chemicals.

Then, referring to FIG. **2**, the material **14** may be decomposed to form a pure or substantially nitride free metal layer **16**. After deposition of on patterned wafers, the layer **16** is decomposed to pure copper, in one embodiment, or pure nickel, in another embodiment, where Ni_3N is used. Methods for decomposing the material **14** include thermal annealing in pure hydrogen gas, diluted hydrogen gas in an inert gas, annealing in NH_3 or nitrogen gas, at temperatures ranging from 200° C. to 500° C., for times ranging between five minutes to 120 minutes. The Cu_3N material **14** may transform into near bulk copper conductivity within about one hour.

In another embodiment, an electron beam, with appropriate diameter and energy, may be used to decompose the Cu_3N into copper. Other thermal decomposition techniques may be used, including rapid thermal annealing in vacuum and joule heating using a resistive underlayer. Non-thermal decomposition may also be used, including ion implantation, ion bombardment, light, and plasma (remote and near) annealing.

In some embodiments, as shown in FIG. **3**, the material **14** may be converted entirely into a pure metal layer **16**. In other embodiments, as shown in FIG. **2**, the conversion may be incomplete, leaving a thin layer of material **14** between the pure metal layer **16** and the material **12**. Thus, the material **14** remains in contact with the first material **12** over a substrate **10**, such as a silicon substrate.

The material **14** may serve as an adhesion layer to the nitrided barrier material **12**. The conversion of the material **14** allows the deposition of two consecutive ALD or CVD layers for barrier and seed, all in one deposition step in some embodiments.

The presence of a nitrided barrier material **12** may also act as a getterer of nitrogen and may not allow the formation of CuN layers in the pure copper film. A preferred embodiment uses ALD TaN as the nitrided barrier with Cu-nitride deposition. In addition, the Cu_3N material may be deposited directly on silicon or carbon doped silicon to form SiCN, which may act as a barrier to copper diffusion. In still another embodiment, the Cu_3N layer is deposited on porous low dielectric constant material and can serve as a dual sacrificial pore sealing/adhesion layer.

Referring to FIG. **4**, in some embodiments, a Cu_3N layer **14*a*** may be used as a sacrificial/morphing non-reflective coating on a copper metal layer **16** to permit further patterning using optical techniques. In such case, a Cu_3N layer **14*a*** may first be deposited and post-treated to pure copper metal layer **16**, as indicated in FIG. **3**. Then a second Cu_3N layer **14*a*** may be deposited over the reflective metal layer **16**. The Cu_3N layer **14*a*** acts as a non-reflective layer for patterning an overlying resist and etching. After the patterning is complete, the Cu_3N layer **14*a*** can act as an adhesion layer or be reverted back to a conductive or pure metal layer.

In a further embodiment, copper and Cu_3N may be used as selective etching layers, or Cu_3N can be selectively etched over copper to produce conductive copper lines.

Moving to FIG. **5**, in accordance with one embodiment of the present invention, an atomic layer deposition metal nitride material **14** may be formed over a nitrided barrier material **12** on top of a substrate **10**, such as a silicon substrate. The material **14** may be selectively converted into pure or substantially nitride free copper metal strip **16***a* by the use of an electron beam E or other methods already mentioned. A nano-patterned metal strip **16***a*, shown in FIG. **6**, may be obtained by placing the nanometer sized (i.e., of a width on the order of a billionth of a meter) electron beam E at exact locations using a reticle or precise beam location. For example, a nanowire may be formed by moving the electron beam over the material **14**. The surrounding unconverted dielectric material **14** can be used as an encapsulating material to avoid line shorting.

In some embodiments of the present invention, it is possible to deposit films with precise thickness and composition control. The deposition of conformal, uniform, and nanometer-sized films may be achieved in some embodiments with a nitrided cap and sidewalls to prevent full line oxidation. Conductive lines or layers may be precisely located in some cases and improved adhesion to silicon or nitrided substrates may be achieved. Also, low reflectivity enabling patterning may be accomplished in some cases. In some embodiments, deposition and patterning of ultra-thin lines may be achieved with width and height less than ten nanometers or to a size enabled by electron beams or scanning tunneling microscopy (STM) resolution.

References throughout this specification to "one embodiment" or "an embodiment" mean that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one implementation encompassed within the present invention. Thus, appearances of the phrase "one embodiment" or "in an embodiment" are not necessarily referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be instituted in other suitable forms other than the particular embodiment illustrated and all such forms may be encompassed within the claims of the present application.

While the present invention has been described with respect to a limited number of embodiments, those skilled in the art will appreciate numerous modifications and variations therefrom. It is intended that the appended claims cover all such modifications and variations as fall within the true spirit and scope of this present invention.

What is claimed is:

1. A method comprising:

forming a second metal nitride on a first metal nitride; and converting the second metal nitride to a metal, wherein said forming the second metal nitride comprises forming one of a copper or nickel nitride layer.

2. The method of claim **1** including converting said second metal nitride to a metal that adheres to said first material better than if said metal were deposited on said first metal nitride.

3. The method of claim **1** including converting said second metal nitride to said metal by the application of energy to said second material.

4. The method of claim **3** including converting said second metal nitride to said metal by the application of heat.

5. The method of claim **1** including forming said second metal nitride of Cu_3N, Cu_4N, or Ni_3N.

6. The method of claim **1** including forming said first metal nitride of a nitride barrier layer.

7. The method of claim **6** including forming said first metal nitride of titanium or tungsten nitride.

8. The method of claim **1** including selectively converting only a portion of said second metal nitride to a metal.

9. The method of claim **8** including using an electron beam to selectively convert only a portion of said second metal nitride to metal to form a nanowire.

10. The method of claim **1** including forming a second metal nitride of copper nitride by atomic layer deposition or chemical vapor deposition.

11. A method comprising:

forming a second metal nitride on a first metal nitride; and converting the second metal nitride to a metal, wherein said converting the second metal nitride to said metal further comprises selectively converting only a portion of said second metal nitride to a metal.

12. The method of claim **11** including forming the second metal nitride of a copper or nickel nitride.

13. The method of claim **11** including forming the second metal nitride of copper nitride by atomic layer deposition or chemical vapor deposition.

14. A method comprising:

forming a second metal nitride on a first metal nitride; and converting the second metal nitride to a metal, wherein said forming the second metal nitride comprises forming a copper nitride layer by atomic layer deposition or chemical vapor deposition.

15. The method of claim **14** including selectively converting only a portion of said second metal nitride to a metal.

16. The method of claim **15** including using an electron beam to selectively convert only a portion of said second metal nitride to metal to form a nanowire.

17. The method of claim **14** including forming said first metal nitride of titanium or tungsten nitride.

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